Niobium-doped Strontium Titanate Electrocatalysts for Oxidative Dehydrogenation of Ethane to Ethylene

Undergraduate Research Thesis

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Abstract

The conversion of ethane to ethylene is an important reaction for industrial use, as ethylene serves as a building block for more complex organic molecules. Current methods of ethylene production are very energy intensive, and do not produce high yields from their starting materials. The purpose of this project is to investigate catalysts for the oxidative dehydrogenation of ethane. Perovskite materials of varying composition—Niobium-doped strontium titanates and niobium/chlorine-codoped strontium titanates—were synthesized by a sol-gel method. The activity of each catalyst was tested in a packed-bed reactor, with results analyzed by gas chromatography. The most active catalysts will undergo further electrocatalytic testing in order to determine their electrical properties. Catalysts with good activity, selectivity, and conductivity could be used industrially in order to replace energy-intensive steam cracking methods for ethylene production with more efficient oxidative dehydrogenation.

Introduction

Ethylene is a very industrially important material. As a basic chemical "building block" ethylene can be used in a variety of processes to produce larger organic molecules, including polymerization to produce plastics like polyethylene. Ethylene serves as a raw material for products like polyvinyl chloride (plumbing and other uses), ethylene glycol (antifreeze), and styrene-butadiene (artificial rubber for tires). The major drawback to ethylene is that it is not available as a raw natural resource, and must be synthesized from other sources. Over 95% of commercially produced ethylene comes from naphtha steam cracking [1]. The problem with steam cracking is that it must occur at high temperatures, around 900 °C [2]. This makes steam cracking the most energy-intensive process in the chemical industry, accounting for about 8% of energy use in the industry worldwide [3].

Ethane is readily available as a component of natural gas, and it is much more naturally abundant than ethylene. Unlike ethylene, however, ethane is a saturated hydrocarbon and thus not reactive enough to be used as a "building block" molecule. One method that has been proposed for converting ethane to ethylene is ODH. Traditional ODH works by feeding oxygen and ethane into a catalytic reactor together, where they react to form ethylene and water according to the following equation:

$$C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O$$

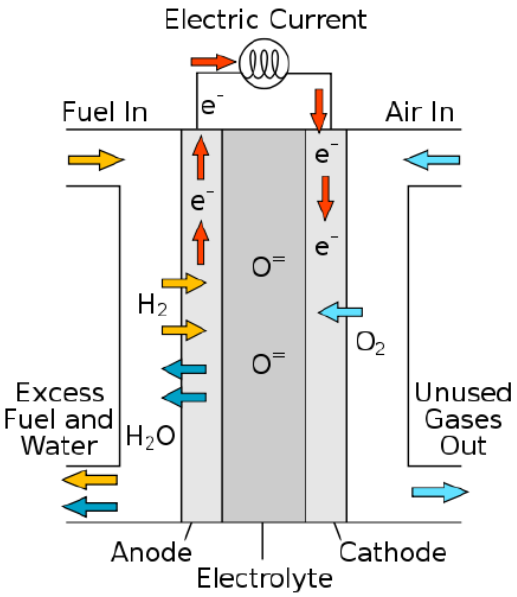

Figure 1: Diagram of a typical SOFC

This is potentially dangerous, however, as it requires mixing ethane and oxygen at elevated temperatures, creating risk of explosion or fire.

Electrocatalytic ODH provides another, safer, and potentially more selective avenue for ethylene synthesis. This process works by, essentially, using a solid oxide fuel cell (SOFC) in reverse. Where an SOFC typically takes advantage of a favorable reaction to produce a current across an

electrolyte cell, the ODH process uses an applied current to drive an unfavorable reaction, in this case ionizing oxygen and reacting it with ethane to strip off two hydrogen atoms, forming ethylene and water, according to the following equations.

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$$

$$C_2H_6 + O^{2-} \rightarrow C_2H_4 + H_2O + 2e^-$$

In order for this process to be carried out successfully, sufficiently active catalysts must be developed. A successful electrocatalyst for ODH would allow for the reaction to be carried out while consuming less energy than steam cracking, and also would improve selectivity, resulting in a higher ethylene yield, approximately 80%, compared to the less than 40% yield for current techniques [3]. Current catalysts for ethane ODH, however, are not efficient enough for widespread industrial use.

The purpose of this project is to investigate the potential for various doped perovskite catalysts to serve as electrocatalysts for ethane ODH. Perovskites are ceramic materials with formula ABO_3, where A and B represent metals. An example of the structure of a cubic perovskite is presented in Figure 2.

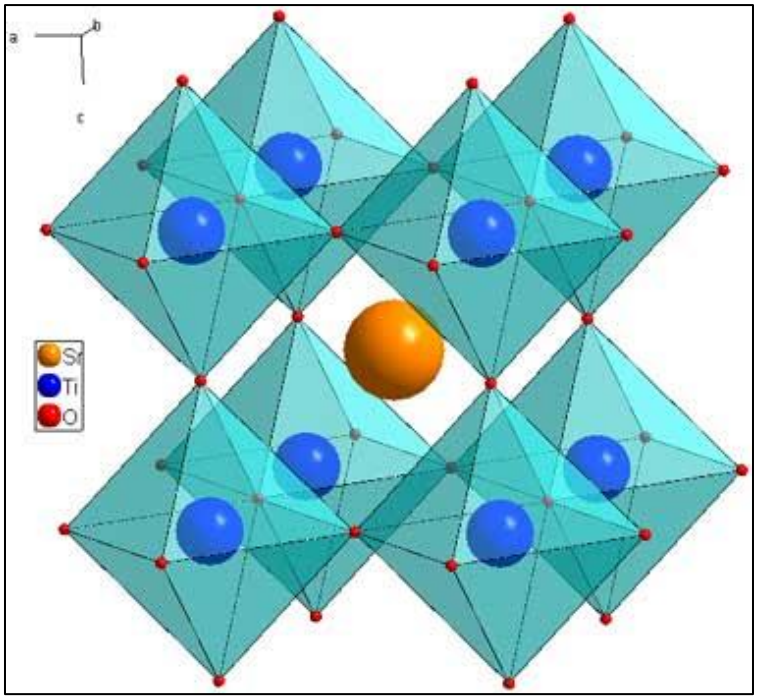

Figure 2: Diagram of $SrTiO_3$ structure, where orange represents strontium, blue represents titanium, and red represents oxygen [4]

A successful ODH catalyst must be both electrically conductive and conductive to oxygen ions. Previous research in Dr. Ozkan's group has focused on lanthanum-doped and lanthanum/chlorine-codoped strontium titanates, and these have shown promise. Lanthanum is an A-site dopant, replacing

strontium in the perovskite structure. Building on this success, this project explored the use of niobium as a dopant in strontium titanates. Unlike lanthanum, niobium is a B-site dopant, replacing titanium in the structure. Niobium-nickel catalysts have proven to have good catalytic activity, which is why niobium was chosen as a dopant [5].

Method

The first step in this project was catalyst synthesis. Previous work in the Ozkan group has resulted in the development of a sol-gel method for synthesizing strontium titanate catalysts, based on a process described by Kao and Yang [6]. The synthesis begins by heating a mixture of ethanol, ethylene glycol, and a stoichiometric amount of titanium isopropoxide to 76 °C in a water bath. To this mixture, a stoichiometric solution of strontium and lanthanum nitrates is added. After this addition, ammonium hydroxide solution is added to the mixture in order to raise the pH to 6. The mixture is then stirred for four hours, resulting in a viscous gel. This gel is then dried overnight at 200 °C, resulting in a brittle black foam. This foam is then ground and calcined at high temperature (1000 °C for 8 hours) to produce a chalky white powder. Finally, the calcined catalyst is ground and stored for later testing.

In order to adapt the synthesis procedure for the production of niobium-doped strontium titanate catalysts, several modifications were made. Initially, niobium ethoxide was used as the niobium source. This material is highly water-reactive, and thus had to be added before the introduction of the metal ion solution. Instead, niobium ethoxide was added along with titanium isopropoxide to the ethanol-ethylene glycol mixture. This minimized formation of niobium oxide and ensured that the desired quantity of niobium was present in the finished catalyst.

In order to further reduce loss of niobium, later syntheses used niobium chloride in place of niobium ethoxide. Since niobium chloride is more stable than niobium ethoxide, it resulted in an easier synthesis procedure, and likely resulted in greater integration of niobium in the catalyst. Niobium chloride is also a solid, which allowed for easier measurement than niobium ethoxide. It is still water reactive, however, so the solid niobium chloride was dissolved in ethylene glycol before proceeding with the synthesis. The lack of a washing step in the synthesis, however,

means that chlorine is likely to remain in the structure of the catalyst after calcination, making these catalysts niobium/chlorine-codoped materials, rather than simply niobium-doped.

Following catalyst synthesis, characterization was performed to ensure that the desired perovskite structure had been achieved. X-ray powder diffraction (XRD) was used to analyze the crystal structure of the catalyst materials. The resultant peak pattern was then qualitatively compared against a known perovskite pattern to ensure that the material appeared to be a cubic perovskite. Any catalysts that exhibited impurity peaks or unexpected diffraction patterns were resynthesized. In terms of catalyst composition, no further characterization was performed beyond the initial stoichiometric measurements of materials. It was assumed that all of the metal species initially added to the precursor would be present in the final catalyst, because no filtration or washing steps were performed in the synthesis.

The final step in the process was packed-bed testing of each finished catalyst material. For this procedure, approximately 100 milligrams of catalyst were loaded into a quartz reactor. A mixture of 4% ethane and 2% oxygen in helium was then flowed over the reactor at temperatures ranging from 400 °C to 600 °C. The outlet stream was sampled with a gas chromatograph and analyzed to determine the composition, and thus the conversion of the reactant feed. A diagram of the testing setup is shown in Figure 3, below.

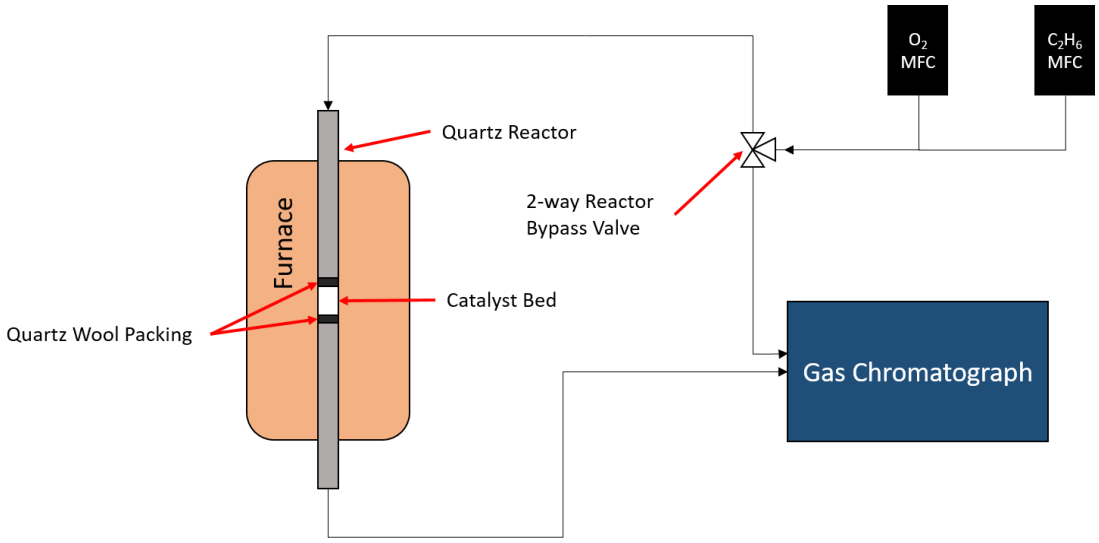

Figure 3: Diagram of packed bed testing setup

Results and Discussion

Characterization

The results of XRD testing are presented below in Figure 4. The four materials tested are as follows: $SrTiO_3$ (ST), $SrTi_{0.95}Nb_{0.05}O_3$ (SNT-5), $SrTi_{0.9}Nb_{0.1}O_3$ (SNT-10), and $SrTi_{0.85}Nb_{0.15}O_3$ (SNT-15). All niobium-doped catalysts were synthesized using niobium ethoxide.

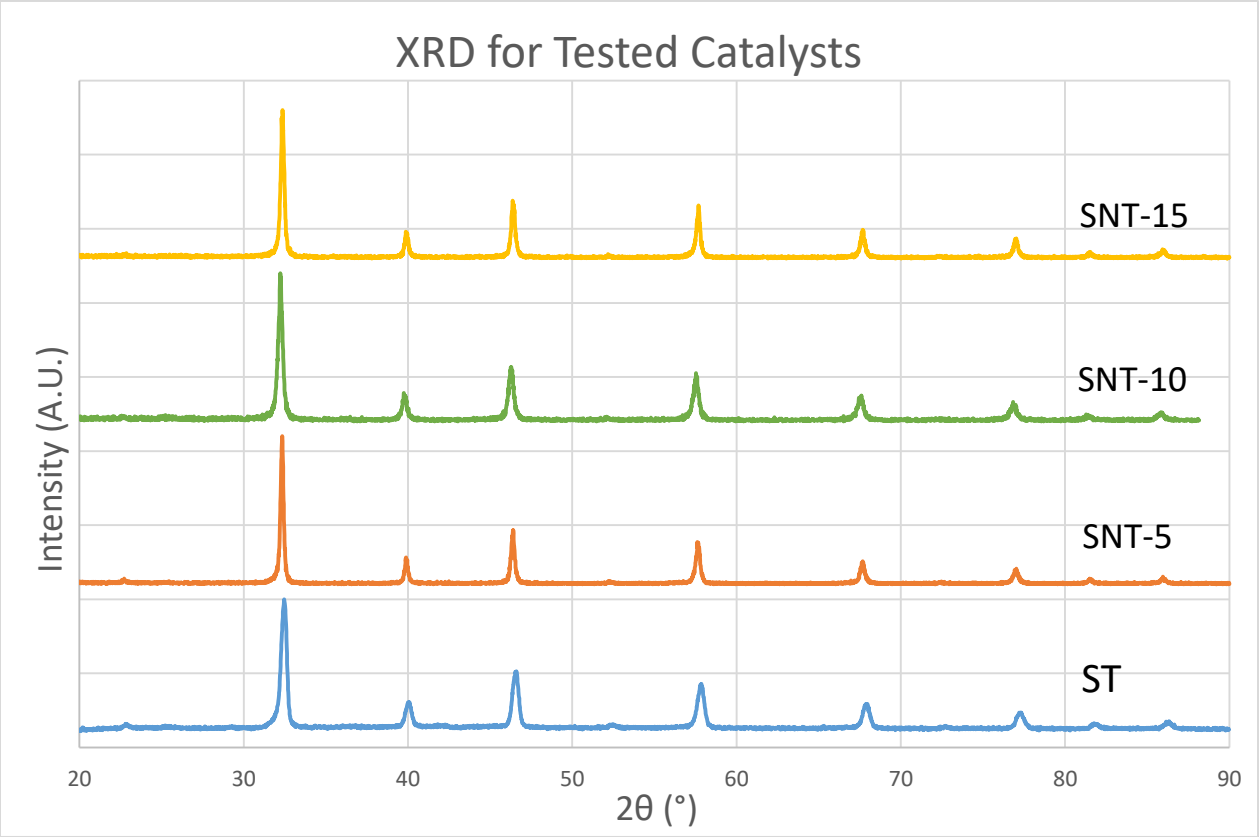

Figure 4: XRD spectra for all catalysts tested.

From these spectra, it can be concluded that all of the materials have the same crystal structure, due to their identical peak patterns. Further, since the ST used is known to be a cubic perovskite, it can be concluded that the niobium-doped materials synthesized also had cubic perovskite structures. There are no notable impurity peaks for any of the materials tested.

Calcination Temperature Investigation

The effects of calcination temperature on the structure of 5% Nb-doped $SrTiO_3$ (SNT-5) were investigated using XRD. Three samples of the same batch of precursor were calcined at different temperatures (800 °C, 900°C, and 1000 °C), and each was tested. The results of these tests are presented in Figure 5 below.

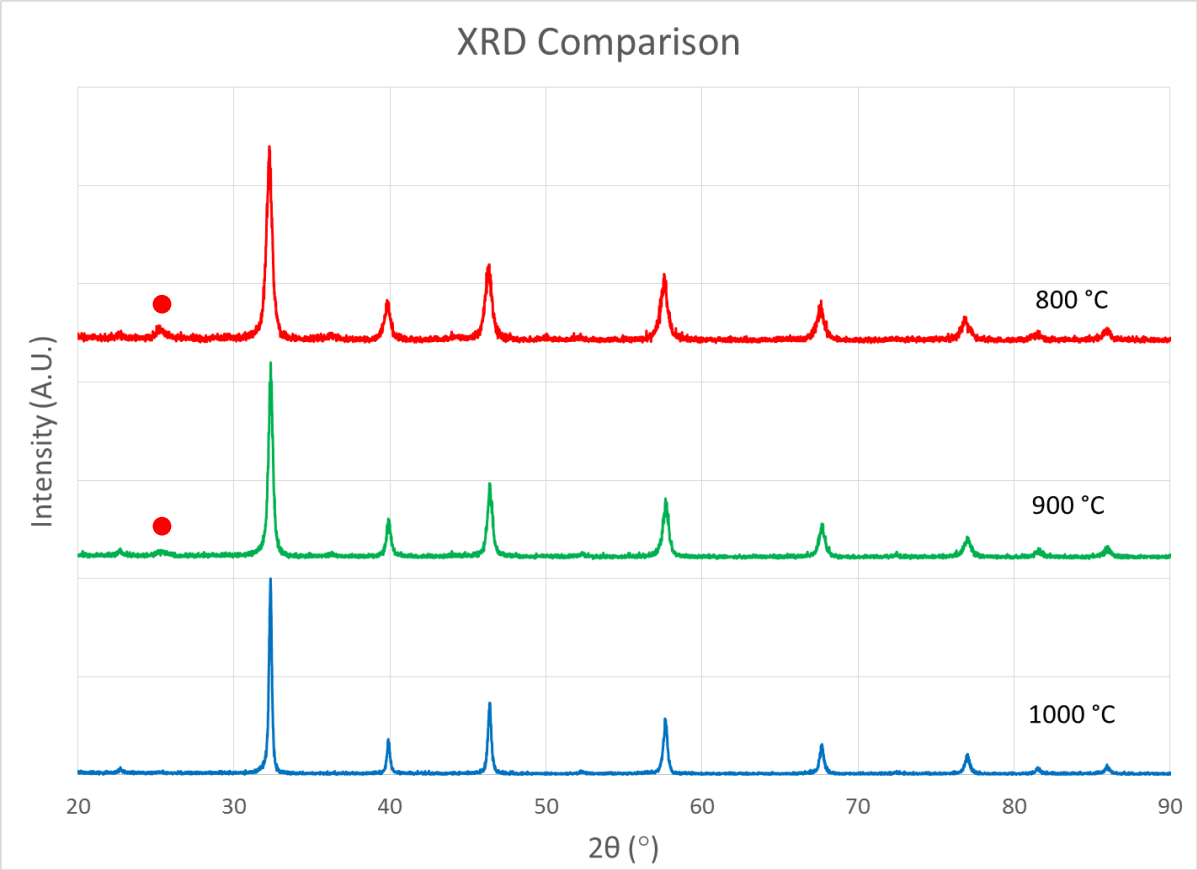

Figure 5: XRD for 5% Nb-doped $SrTiO_3$ calcined at three temperatures

From these results, it can be seen that increasing calcination temperature results in a sharper XRD pattern, which indicates that the catalyst is more crystalline. The noise seen in the patterns for the catalysts calcined at lower temperature arises from irregularities in their crystal structure. There is also an impurity peak at a 2θ angle of approximately 25°, marked in the figure with a red dot, which appears at 900 °C and becomes more prominent at 800 °C. The absence of this peak in the sample calcined at 1000 °C is indicative of its purer perovskite structure. From these results,

it can be concluded that a calcination temperature of 1000 °C results in a catalyst with a more regular crystalline perovskite structure.

Packed-bed Testing

Packed bed tests were performed using the four catalysts discussed in the Characterization section. This ensured that niobium was the only dopant, and that no chlorine was incorporated into the structure. All catalysts were calcined at 1000 °C for 8 hours. In order to determine the effectiveness of the catalysts, three parameters were considered: ethane conversion, ethylene yield, and carbon dioxide yield. Ethylene yield is an indicator of how well the material catalyzed the desired ethane to ethylene ODH reaction. Ethane conversion is a measure of the overall activity of the catalyst, while carbon dioxide yield is an indicator of how much of the ethane was consumed by combustion, which is the major side reaction that competes with ODH.

The ethane conversion results are presented in Figure 6, below.

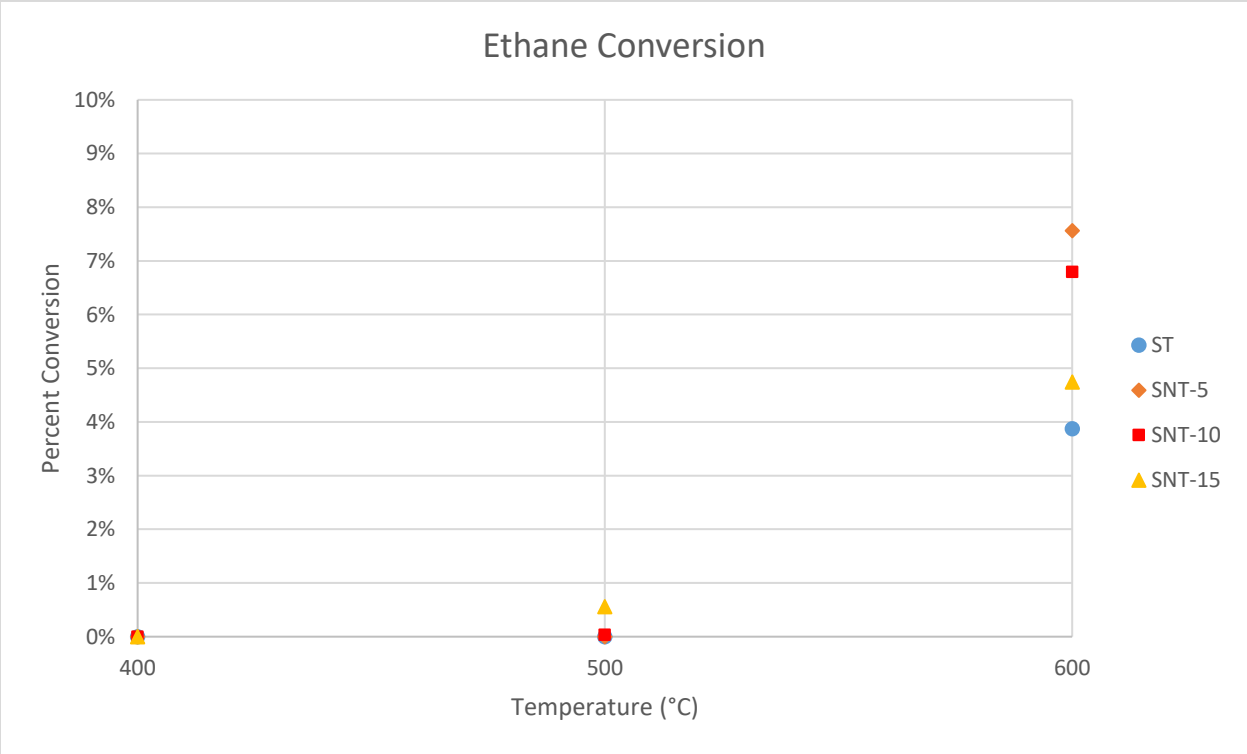

Figure 6: Ethane conversion for all catalysts

These results show that, for all catalysts, there is little to no catalytic activity at temperatures of 400 °C and 500 °C. Surprisingly, there did not appear to be any ethane conversion at these temperatures, indicating that neither ODH nor any side reactions were occurring. At 600 °C, however, there is some conversion of ethane for all catalysts. SNT-5 and SNT-10 produce the highest conversion, which indicates that niobium doping likely increases catalyst activity—up to a certain doping load—for strontium titanate catalysts.

The results for ethylene yield testing are presented in Figure 7, below.

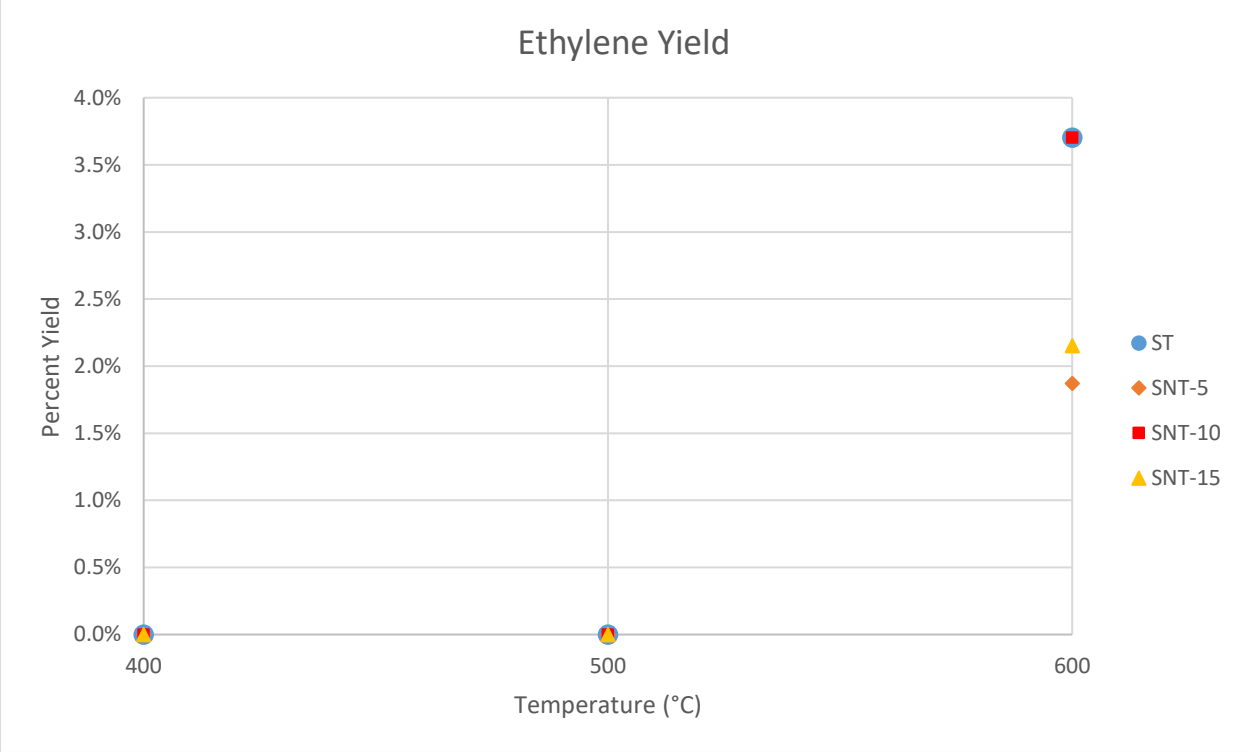

Figure 7: Ethylene yield for all catalysts

The ethylene yield values were calculated according to the following formula:

$$Yield = \frac{(Outlet\ \%\ ethylene - Inlet\ \%\ ethylene)}{Inlet\ \%\ ethane}$$

This data clearly shows that the highest ethylene yield in this temperature range is achieved at a temperature of 600 °C, using both ST and SNT-10. This indicates that the optimal ethylene yield may be obtained with a niobium doping load somewhere between 5% and 15%, as both SNT-5 and SNT-15 had inferior performance to SNT-10 and undoped ST.

Finally, carbon dioxide yield was calculated according to the following formula:

$$Yield = \frac{(Outlet\ \%\ CO_2 - Inlet\ \%\ CO_2)}{2 \cdot (Inlet\ \%\ ethane)}$$

The results of this calculation are presented in Figure 8, below.

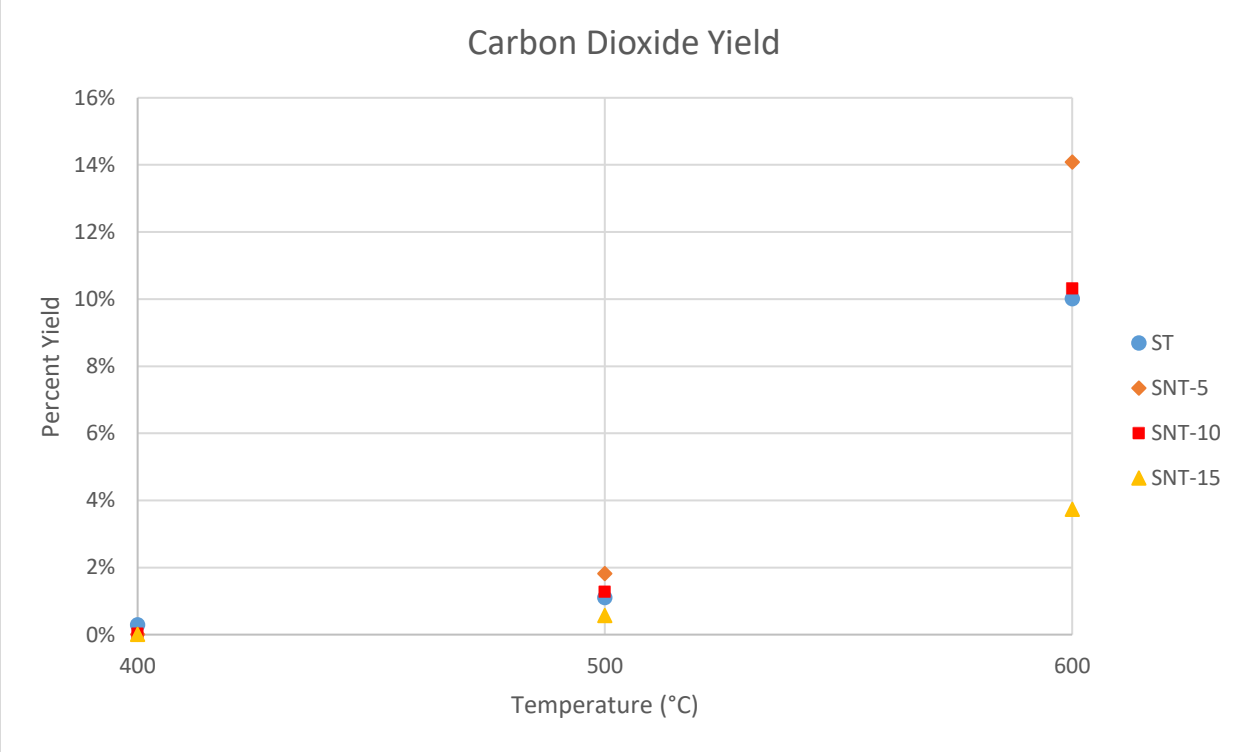

Figure 8: Carbon dioxide yield for all catalysts

It may be noted that, in some cases, CO_2 was produced without any ethane conversion. The most likely cause for higher CO_2 yields than ethane conversions is the presence of unknown impurities in the feed gas cylinders, which react to form CO_2.

This data shows that, at 600 °C, SNT-15 has a much lower carbon dioxide yield than other catalysts. This indicates that SNT-15 is selective towards ODH at this temperature, which is a desirable characteristic. The selectivity of each catalyst at 600 °C was determined according to the following formula

$$Selectivity = \frac{\%\ yield\ ethylene}{\%\ yield\ CO_2}$$

The results of this calculation are presented in Table 1, below.

Table 1: Ethylene to CO_2 selectivity for all catalysts at 600 °C

Catalyst	Selectivity
ST	0.37
SNT-5	0.13
SNT-10	0.36
SNT-15	0.58

Surprisingly, SNT-5 is much less selective than undoped ST, but subsequent increases in doping load appear to increase catalyst selectivity. Overall, SNT-15's combination of acceptably high ethane conversion and selectivity towards ethylene production makes it a strong candidate for further investigation as to its suitability as a catalyst for ODH.

Future Work

Further packed-bed testing should be performed, in order to confirm observed trends. First, these catalysts should be tested at higher temperatures, in order to determine what their optimal operating temperatures are. Preliminary tests at 700 °C and 800 °C showed promising results for several materials. Chlorine-doped versions of these catalysts should also be tested. Previous research on lanthanum-doped STs found that chlorine doping resulted in more active catalysts. If chlorine co-doping in niobium-doped STs is similarly advantageous, then they should become the focus of this research. Their relative ease of synthesis, coupled with the lower price of niobium chloride relative to niobium ethoxide, makes niobium and chlorine co-doping particularly attractive.

The next step in this investigation should be conductivity testing. While packed-bed activity is a useful measure of catalyst potential, it is vital that any material used in an ODH reactor be electrically conductive. Following this testing, materials that have shown both good packed-bed activity and conductivity should be selected for electrocatalytic testing. This will require building a bench-scale ODH reactor, consisting of an electrolyte cell coated with a thin layer of catalyst material. This test will be used to examine the actual viability of these catalysts for ODH. Success

in electrocatalytic testing will indicate that a catalyst could be used for industrial ODH, and catalysts that show promise in this test should be selected for scale-up testing.

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